Hysteresis during Cycling of Lithiated Silicon Electrode

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Similar to the nickel hydroxide electrode[1], the silicon electrode exhibits hysteresis during electrochemical lithiation and delithiation, with potential during lithiation being lower than that during delithiation, even at low rates. We present data to show that the potential obtained at any state of charge (SOC, z), as well as how lithiation and delithiation occurs from that SOC depends on the cycling history of the electrode. The implication of this phenomenon is that the potential of silicon-based Li ion batteries at any instant (regardless of the prior charge/discharge rates) cannot be used as an indication of the SOC of the cell.

The cycling behavior of the lithiated silicon electrode conforms to all of the hysteresis theorems originally developed based on domain theory for adsorption and magnetism[2, 3]. For example, any departure from the lithation boundary curve via scanning curves (see Fig. 1-A) takes the system to the upper intersection point (z = 1) and any departure from the delithiation boundary curve takes the system to the lower intersection point (z = 0) (Fig. 1-A). If scanning is reversed at any point in between, the system will return to its original departure point in the boundary curve, wiping out the memory (Fig. 1-B). Such loops generated for a set of potentials (V_A, V_B) and a corresponding set of SOCs (z_A, z_B) appear symmetric with similar area. Also, a point in the area enclosed by the upper and the lower boundary curves can be reached in a number of ways (e.g., point P in Fig. 1-C). If the system is taken through a series of oscillations of decreasing SOC amplitude, the systems moves towards the point where the previous reversal occurred (inset in Fig. 1-D).

From a hysteresis standpoint, this talk will discuss the implications of using silicon-based anodes in lithium-ion batteries. In addition, we will also present our attempts to model this electrochemical hysteresis using first principles.

References

1. V. Srinivasan, J. W. Weidner and J. Newman, *J. Electrochem. Soc.,* **148,** A969, (2001)
2. D. H. Everett, and H. W. Smith, *Trans. Faraday Soc.*, **50,** 187, (1954)
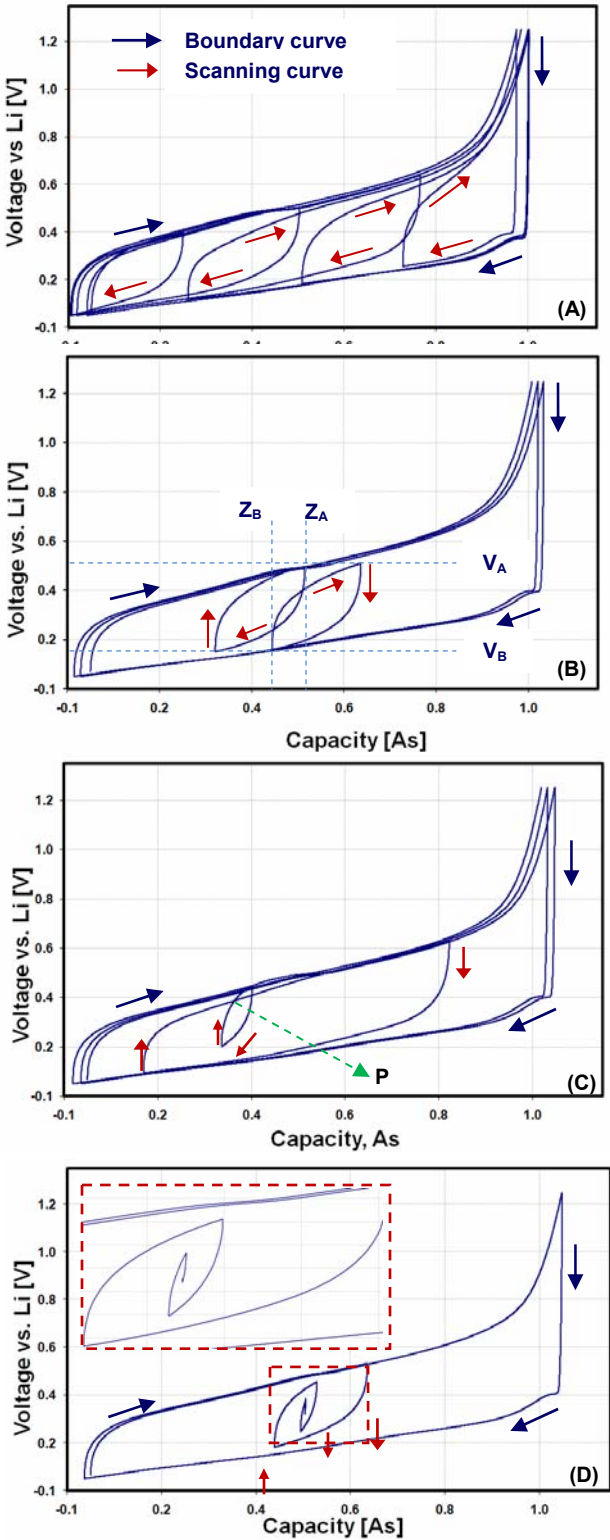3. D. H. Everett, *Trans. Faraday Soc.*, **50,** 1077, (1954)

Figure 1: Experimental validating of theorems 2 and 3 (A), theorems 4a, 4b, and 5 (B), theorem 6 (C), and theorem 7 (D).